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Determination of ^{129}I in aerosols using pyrolysis and AgI-AgCl coprecipitation separation and Accelerator Mass Spectrometry measurement

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Highlight

1. A method for determination of ^{129}I in aerosols was established using pyrolysis and AgI-AgCl coprecipitation separation coupled to AMS measurement.
2. The required sample size is reduced by a factor of 3 using only 0.2 mg ^{127}I carrier instead of 1.0 mg carrier in the previous work.
3. Pyrolysis behaviors of different iodine species were discussed.

Abstract

Airborne radioactive iodine is a key concern for transport and dispersion of radioactive contamination and radiation exposure evaluation during nuclear accidents and nuclear emergency preparedness. Long-lived ^{129}I in aerosols is vital for reconstruction of level and distribution of short-lived and highly toxic ^{131}I, as well as understanding the knowledge of atmospheric dispersion of iodine. However, aerosol ^{129}I concentration is difficult to measure due to its low concentration in the areas remote from nuclear pollution sources. In this study, a novel method for determination of ^{129}I in aerosols collected on glass fiber filter was developed using high-temperature pyrolysis and AgI-AgCl coprecipitation for its separation coupled to highly sensitive accelerator mass spectrometry (AMS) for its measurement. It is worth to note that even though the pyrolysis behaviors of various iodine species were different, all iodine can be quantitatively recovered. Iodate can be released from the aerosols by decomposition to iodine at a temperature over 500°C. The chemical yield of iodine in the pyrolysis is 81.5 ± 5.8%. The detection limit for ^{129}I in aerosol is 1.3×10^{4} atoms/m^3, allowing to use three times less aerosol sample size than that using the alkaline-ashing separation coupled to solvent extraction method. For aerosol samples collected in Asia with $^{129}I/^{127}I$ ratio of (0.1-10) $\times10^{-9}$, a volume of 1000 m^3 air is sufficient for determination of ^{129}I. The developed methods have been applied to analyze the aerosol samples collected in Xi'an, an inland Chinese city, for iodine isotopes. It was observed that ^{129}I concentrations range within (0.38-5.19) $\times10^{5}$ atoms/m^3, and $^{129}I/^{127}I$ ratios of (21.7-252) $\times10^{-10}$, which is comparable to those collected in Japan before the Fukushima nuclear

accident and Spain, while much lower than those in Northern Europe.

Keywords

^{129}I, aerosol, accelerator mass spectrometry, coprecipitation, pyrolysis

1. Introduction

Iodine presents in the atmosphere in gaseous and particulate associated species. Residence time of iodine in the atmosphere varies from a few minutes to tens of days for gaseous organic and inorganic compounds and particulate-associated species [1]. Iodine is a key climate-related element. New molecular-scale evidence indicates that aerosol particle formation is related to sequential addition of HIO_3 [2]. Airborne iodine is intensively focused not only to study geochemical circulation of iodine, but also to investigate transportation of radioactive iodine released from nuclear facilities and nuclear accidents. After the Fukushima accident in 2011, a long-lived radioiodine, ^{129}I, has been extensively investigated in soil, air and water systems [3–5]. ^{129}I in aerosols has been determined for reconstruction of short-lived radioactive ^{131}I [6–8], and investigation of atmospheric circulation in high altitude locations, and environmental safety around nuclear facilities [9–11].

Even though analytical methods for determination of ^{129}I in aerosols have been reported, large sample size and time-consuming analytical procedure are the challenge for determination of low-level ^{129}I concentrations in aerosols. ^{129}I concentrations in the atmosphere range from 10^4 atoms/m^3 in Asia to 10^6 atoms/m^3 in northern Europe [12,13]. The conventional methods generally requires a few hundreds to thousands cubic meters of air for determination of ^{129}I in aerosols. According to our previous method of alkaline ashing followed by solvent extraction [14], about 3000 m^3 air is required for analysis of aerosol ^{129}I concentrations in areas less effected by nuclear facilities in Asia. However, large sample size is neither accessible nor easy to prepare.

Two methods are commonly used to separate iodine from filter medium. One is extraction using NaOH [15,16], but our previous work suggests that this method cannot

completely leached iodine from filter [14], which will underestimate iodine concentration in aerosols. Another method is ashing in alkaline medium [14], however, this method is not suitable to analyze the aerosol collected onto glass or quartz fiber filter which formed melt cake prevent from leaching out of iodide afterward. After iodine is released and trapped by alkaline solution, about 1-2 mg stable iodine carrier is often added to make further purification by solvent extraction using chloroform or carbon tetrachloride. However, the addition of iodine carrier will decrease $^{129}I/^{127}I$ ratio of the sample target for AMS measurement. The required sample size can be reduced by decreasing amount of iodine carrier spiked. A carrier-free and later modified with addition of small amount of iodine carrier were developed for this purpose [17,18].

Pyrolysis coupled to AgI-AgCl coprecipitaiton have been developed for separation of iodine from solid sample [17], this method is much efficient and successfully applied for analysis of soil, sediment and vegetation samples. This work aim to apply this method for analysis aerosol samples collected on glass or quartz fiber filter. For this purpose, two issued have to be investigated: 1) the behavior of different species of iodine in samples, to clarify whether all iodine species can be decomposed and separated from aerosol samples during pyrolysis, in particular high oxidation state, iodate, becasue iodine occurs as different species in aerosols, such as iodide, iodate, organic iodine (humic substance associated iodine) and iron/manganese oxide associated iodine; 2) the key issue to reduce the required sample size for simplifying sample preparation. With this investigation, an analytical method for determination of ^{129}I in aerosols using pyrolysis coupled to AgI-AgCl coprecipitation and AMS measurement will be established. The method will be demonstrated by analysis of aerosol samples collected in Xi'an, an inland Chinese city, for ^{129}I concentrations and $^{129}I/^{127}I$ ratios.

Experiment

1.1 Chemicals and standards

All used chemicals are analytical reagent and guaranteed reagent grades and were purchased from Sinopharm (Shanghai, China) and Kermel (Tianjin, China). Deionized

water (18.2 MΩ cm) produced by a pure water system (PALL corporation, USA) was used to prepare all solutions.

^{129}I standard solution (NIST-SRM-4949c) was purchased from National Institute of Standards and Technology (Gaithersburg, MD, USA). The Woodward iodine (WWI) crystal was obtained from the Woodward Co., Ltd (USA). The single element ICP-MS standards, ^{127}I and ^{133}Cs standard solutions (1000 μg/mL) were purchased from NCS Testing Technology Co., Ltd. (Beijing, China).

2.2 Sampling and sample preparation

The aerosol samples were collected on glass fiber filter (200 mm×220 mm, Tianhong Instrument Ltd., Wuhan, China) using a high-volume sampler with a flow rate of 1.5 m^3 min^{-1} on the roof (440 m asl and 12 m above the ground) of the Xi'an AMS center (34°13'25"N, 109°0'0"E) in Xi'an, China. Iodine was separated from the aerosol filter using pyrolysis method (Figure 1 and S1). The aerosol samples were cut into small pieces, and placed into a corundum boat. ^{125}I in the form of iodide or iodate was added as chemical yield tracer to investigate the influence of iodine species on chemical yield. Iodine in the samples was released as gaseous form at high temperature in the atmosphere of nitrogen and oxygen gases in a tube furnace [17,19]. The protocol of combustion is shown in Table S1. In brief, the temperature of the furnace was first increased from room temperature to 250°C within 20 min, and dwell for 10 min. A slower ramp rate of temperature, 5°C/min from 250°C to 400°C is used for allowing complete combustion of organic matter and slow production rate of carbon dioxide to ensure the tube pressure in a safe scope. Both nitrogen and oxygen gases were used before 400°C, for which the former gas acts as a protective and dilution gas and the latter one as an oxidation gas. After dwelling at 400°C for 20 min, the temperature is further increased to the pyrolysis temperature and dwells for 1-3 hours to release iodine. Because organic matter has been burnt completely, only oxygen gas is used in the pyrolysis step for oxidation of iodine. The pyrolysis temperature of 700, 800 and 900°C and combustion time of 1, 2, 3 hours were investigated for their influence on chemical yield of iodine species.

The released iodine was trapped into a solution containing 0.5 mol L^{-1} NaOH and 0.02 mol L^{-1} $NaHSO_3$. An aliquot of solution (1.0 mL) was taken for determination of ^{127}I using ICP-MS. Another 1.0 mL solution was taken to a tube and counted for ^{125}I using a NaI gamma counter (Model FJ2021, Xi'an Nuclear Instrument Factory, China) to calculate the chemical yield of iodine during combustion. After gamma measurement, the sample solution was combined with the original solution, and 0.2 mg ^{127}I carrier was added to the trap solution. For procedure blank samples, 0.5 mg chloride (as NaCl) was added. 1 mL of 0.5 M $NaHSO_3$ was used to reduce iodate to iodide. The solution was adjusted to pH < 2 by 3 M HNO_3. 1 mL 0.5 M $AgNO_3$ solution was directly added to the solution to precipitate iodine as AgI-AgCl coprecipitation. The formed AgI-AgCl precipitate was washed once with 3 M HNO_3 to remove Ag_2SO_3 and Ag_2SO_4, then washed with deionized water once and 5-20% ammonium hydroxide once to remove excessive AgCl, and finally rinsed twice with deionized water. After centrifugation, the AgI-AgCl coprecipitate was ready for AMS measurement. The procedural blank was prepared using a blank glass fiber filter with the same procedure as that for the samples.

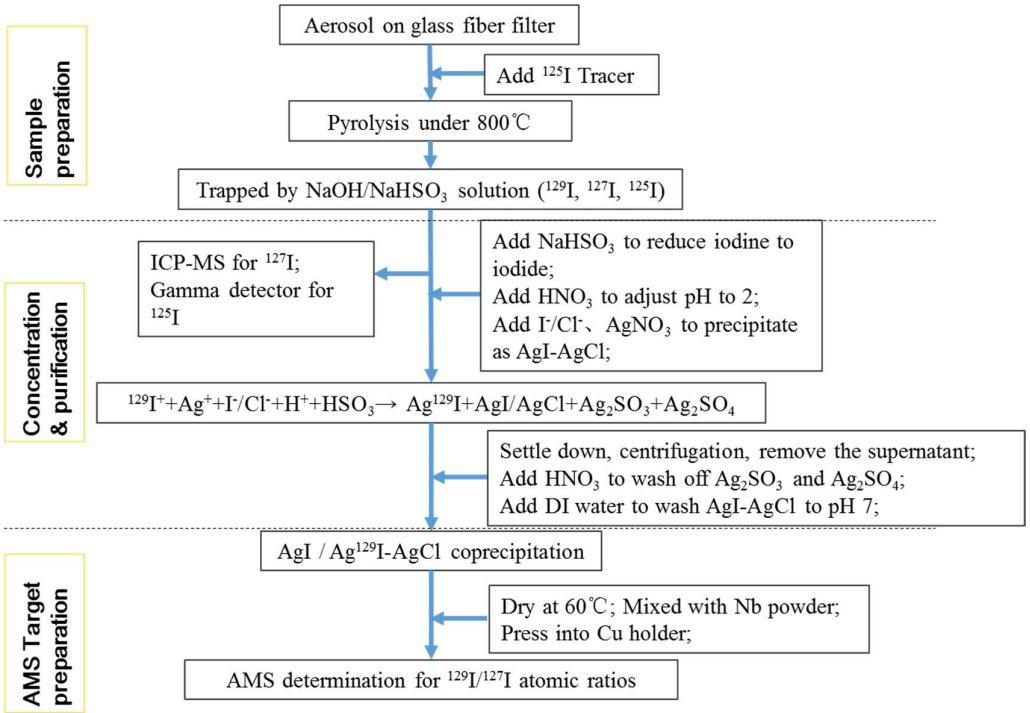


Figure 1. Flowchart of aerosol preparation for determination of ^{129}I using AMS

2.3 Preparation of AgI and AgI-AgCl standards

^{129}I standards were prepared as AgI precipitate and AgI-AgCl coprecipitate to investigate AMS responses to ^{129}I and ^{127}I in the targets, as well as the influence of chloride addition. An ^{129}I solution with ^{127}I concentration of 1.00 mg/mL and $^{129}I/^{127}I$ atomic ratio of 1.072×10^{-10} was prepared by dilution of ^{129}I standard solution (NIST-SRM-4949c) with a ^{127}I solution prepared from Woodward iodine (Woodward company, USA) with $^{129}I/^{127}I$ atomic ratio of 2×10^{-14}. For preparation of the AgI precipitate standard, iodine in the ^{129}I solutions was transformed to iodide using 0.1 mL 0.5 M $NaHSO_3$ at pH<2 and precipitated as AgI by adding 1 mL 0.5 M $AgNO_3$. After centrifugation, the AgI precipitate is ready for use. For preparation of the AgI-AgCl coprecipitate standard, iodine in the ^{129}I solutions was transformed to iodide using 0.1 mL 0.5 M $NaHSO_3$, mixed with chloride in a mass ratio of 1: 5 for I/Cl, and precipitated as AgI-AgCl. After centrifugation, the AgI precipitate and coprecipitate were washed once and rinsed twice with deionized water.

2.4 AMS and ICP-MS determination of ^{129}I and ^{127}I

The AgI precipitate and AgI-AgCl coprecipitate were completely dried at 70°C, then mixed with Nb metal powder (99.9%, 325 mesh, Alfa Aesar, USA) in a mass ratio of 1:5 and pressed into bronze target holders. ^{129}I in the target was measured using a 3MV AMS in the Xi'an AMS Center (Table S2) [17]. Negative ions of iodine are sputtered out from the holder by cesium ion source. The extracted ions are guided to the injector comprising of an electrostatic analyzer and a bouncer magnet, which preliminarily separate ^{129}I and ^{127}I from other ions. Both negative iodine ions are pre-accelerated and sequentially injected to the tandem accelerator, where the outer electrons of iodine isotopes are stripped off by the filled Ar gas. A voltage of 2.5 MV is applied for measurement of $^{129}I/^{127}I$ ratio. The +5 charge state of iodine ion is selected and extracted from the accelerator by a magnetic analyzer. Then, ^{127}I is measured as a current by a Faraday cup immediately after the analyzer. ^{129}I ions is further analyzed by a 65° electrostatic analyzer and a 30° magnetic analyzer for energy and mass analysis. ^{129}I is finally measured as counts by a gas ionization detector filled with sulfur

hexafluoride (SF_6) gas. $^{129}I/^{127}I$ ratios of the iodine carrier (WWI) are determined to be less than 2×10^{-13}.

Due to high salinity, the trapping solution was diluted by a factor of 20-50 with 1% $NH_3\cdot H_2O$, and analyzed for ^{127}I concentration by ICP-MS (Agilent 8800, USA) using the mode of single quadrupole and no dynamic collision-reaction gas (parameters shown in Table S3). Cs^+ (CsCl) was used as an internal standard in the ICP-MS measurement of iodine. The sensitivity of ^{127}I is 250 Mcps per 1 mg/L of iodine, and the instrumental detection limit is 0.002 μg/L for ^{127}I.

2. Results and discussion

3.1 Optimization of pyrolysis temperature and time

The influence of pyrolysis temperature from 700°C to 900°C on chemical yield of iodine has been investigated. The analytical results show that the chemical yields of iodine vary from 65.9% at 700°C to 82.9% at 800°C for three hours (Table 1). Further increasing temperature to 900°C cannot increase the chemical yield of iodine (79.4%). Therefore, the pyrolysis temperature of 800°C is chosen as the optimal condition. We have observed that using the same analytical procedure with pyrolysis temperature of 800°C, the chemical yield for all types of soil samples reaches 95%-100% [19]. The relatively lower chemical yield for aerosol samples compared to soil sample might be attributed to the matrix effect. For the convenience of sample preparation for ^{129}I using pyrolysis method, inorganic filter, such as glass and quartz fiber filters, are preferred for collection of aerosols, because organic filter can produce carbon dioxide to use this method. After pyrolysis, the soil sample is still in powder form, while the glass fiber was melt and become a bulk of glass cake, which might wrapped a small portion of iodine, up to 17%, and cannot be released out. This is also proved by an experiment using blank glass fiber filter with addition of ^{125}I tracer to the filter surface, the observed chemical yield of ^{125}I in the blank glass fiber filter was also less than 85%. There is one way to solve this problem by unfolding completely the aerosol filters. However, this is not feasible due to the limited space of sample holders and the work-tube of the combustion system.

Table 1 Effect of pyrolysis duration on chemical yield of iodine in aerosol on glass fiber filter

No	Temperature, °C	Pyrolysis time, h	Chemical yield in each hour, % (n=4)	Total chemical yield, %
1	700	1	64.6 ± 16.4	65.9 ± 17.0
2	700	2	0.8 ± 0.3	
3	700	3	0.5 ± 0.3	
4	800	1	81.4 ± 5.8	82.9 ± 6.7
5	800	2	0.9 ± 0.6	
6	800	3	0.6 ± 0.3	
7	900	1	77.5 ± 4.7	79.4 ± 5.5
8	900	2	0.9 ± 0.4	
9	900	3	0.9 ± 0.4	

With extended pyrolysis time from 1 hour to 3 hours, 64.6% - 81.4% of iodine was collected in the trapping solution within one hour for pyrolysis temperature of 700, 800 and 900°C, and only less than 2% of iodine is released in the following two hours. Therefore, one hours is chosen as the optimal pyrolysis time.

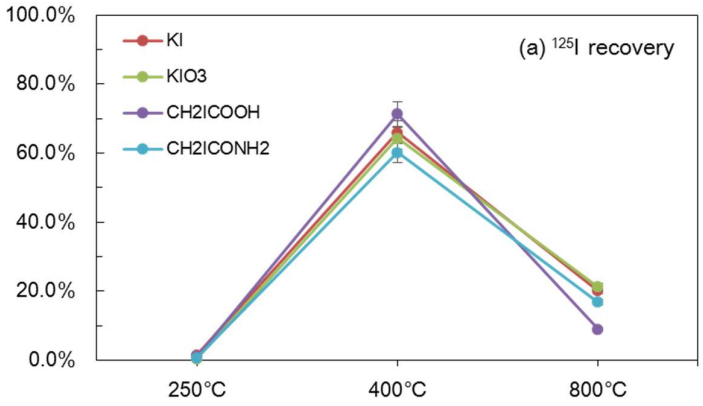
Under the optimal combustion conditions, pyrolysis temperature of 800°C for one hour, the chemical yield of iodine is 81.4 ± 5.8% for aerosol samples on glass fiber filter, which is sufficient for AMS measurement.

3.2 Effect of iodine species on its chemical yield

In our early studies [20], iodide-125, a reduced state, was used as yield tracer, which could be oxidized to gaseous I_2 by oxygen at a high temperature. In this work, iodate-125, an oxidation state, was investigated whether it can be also transformed to gaseous form and then trapped by trapping solution using ^{125}Iodate as tracer. The results shows that the chemical yields (n=4) of iodine in the pyrolysis were 88.3 ± 1.3% and 89.6 ± 0.1% for iodide-125 and iodate-125, respectively, indicating that there is no influence of iodine species in samples on chemical yield during combustion under 800°C for one hour.

3.3 Behavior of ^{125}Iodide tracer and ^{127}I reagents in pyrolysis process

Iodine exist as different species in the sample, only single species of ^{125}I used as yield tracer might not represent all species of iodine in the sample, causing an uncertainty in the ^{129}I and ^{127}I concentration calculated based on the recovery of ^{125}I tracer. During pyrolysis procedure, the influences of temperature on chemical yield of iodide-125 and ^{127}I in four iodine reagents were investigated. The results (Figure 2) indicate that 60.2-71.4% of ^{125}I can be recovered at 400°C, further increased temperature to 800°C and remained for 1 hour, 9-21.3% more ^{125}I can be recovered. Below 250°C, less than 1.6% of ^{125}I can be released. It is obvious that pyrolysis behavior of ^{125}I is hardly influenced by the added iodine reagents. In contrast, in the different reagents, pyrolysis behavior of ^{127}I is apparently different. In particular at 400°C, recovery of ^{127}I decreased from 80.4% to 35.6%, following the order of $CH_2ICOOH > CH_2ICONH_2 \approx KI > KIO_3$, whereas, an inverse order of chemical yield (10.5-55.0%) was observed when further increased temperature to 800°C and remained for one hour. This is related to the reaction of iodine reagents with oxygen under high temperature. Organic iodine species, such as iodoacetic acid are easier than inorganic iodine to react with oxygen and released from the sample.



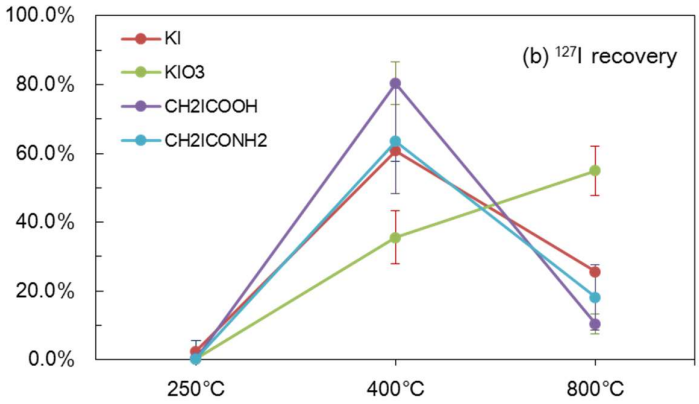


Figure 2. Pyrolysis behavior of ^{125}I tracer in the form of iodide (upper panel) and ^{127}I in the form of potassium iodide, potassium iodate, iodoacetic acid and iodoacetamide (bottom panel).

Even though pyrolysis behaviors of the four iodine species are different, there is only slight influence of iodine species on total chemical yield (Figure 3). However, total chemical yields based on ^{125}I are systematically lower than those of ^{127}I. Chemical yield based on ^{125}I tracer in the form of NaI can well represent the chemical yield of ^{127}I in the form of KI and CH_2ICONH_2 with relative uncertainty less than 5.5%. Whereas bigger relative uncertainty (12-17.6%) can be found in the case of KIO_3 and CH_2ICOOH, which can be attributed to different physicochemical properties and reaction rates of these two iodine reagents from those of KI. Iodate should not be transformed to gaseous I_2 by reaction with oxygen. However, it is found that potassium iodate (KIO_3) and sodium iodate ($NaIO_3$) can be decomposed into potassium iodide and sodium iodide and oxygen under 560°C and 500°C, respectively [21,22]. Under the optimal pyrolysis temperature in this work (800°C), iodate can be decomposed to iodide and oxygen, then iodide can be oxidized to gaseous I_2 that will be released and trapped in a trapping solution. In addition to iodide and iodate, iodine occurs in aerosols as organic iodine (such as those associated to humic-like substances) and metal oxides combined iodine [6,13]. For organic iodine species, it is easy to be decomposed under high temperature in the optimal conditions. For metal oxides associated iodine, such as iron oxide and manganese oxide, iodine is generally absorbed on these minerals, and unlikely composition of crystal lattice, which is readily separated from aerosol matrix under pyrolysis. Furthermore, iron oxide and manganese oxide can be reduced to metal

iron and manganese, respectively, by carbon, carbon monoxide and hydrogen. During these reactions of iron and manganese oxides, iodine also can be released.

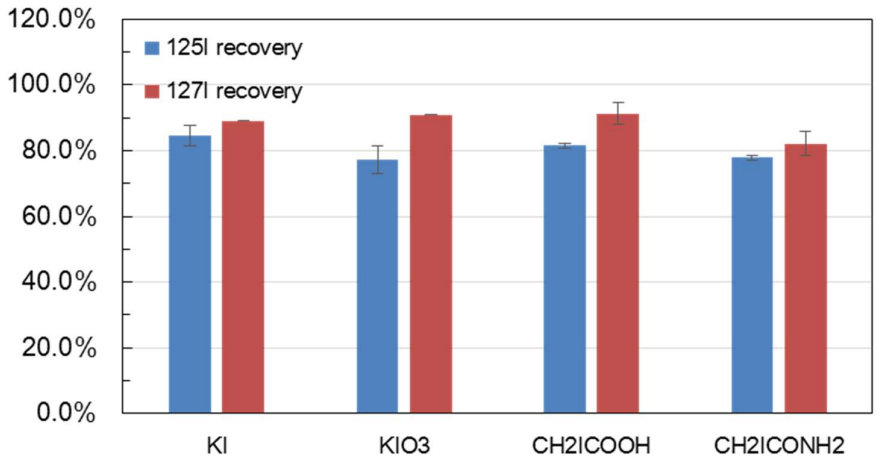


Figure 3. Comparison of chemical yields between ^{125}I tracer and ^{127}I reagents for potassium iodide, potassium iodate, iodoacetic acid and iodoacetamide

Equations (1) – (3) summarize the reactions of organic iodine, iodate and iodide with oxygen under high temperature.

$$RI + O_2 \xrightarrow{800℃} I_2 + CO_2 + H_2O \text{ (R=organic group)} \quad (1)$$

$$KIO_3/NaIO_3 \xrightarrow{560℃/500℃} KI/NaI + O_2 \quad (2)$$

$$2I^- + O_2 \xrightarrow{\Delta} I_2 + O^{2-} \quad (3)$$

In fact, it is scarcely possible to make iodine specie of tracer completely same as those in real sample owing to the complexity of iodine species in the environmental samples. Therefore, the uncertainty of results resulted from difference in iodine species of ^{125}I tracer and ^{127}I and ^{129}I in real environmental samples has to be taken into account in sample preparation.

3.4 AMS measurement of ^{129}I in AgI-AgCl coprecipitation targer of the aerosol samples

For separation of trace amount of iodine from the solution and preparation of solid target of iodine for AMS measurement of ^{129}I. we have proposed a AgI-AgCl co-precipitation method. In this method, chloride was added as carrier to precipitate AgI as AgI-AgCl copreciptiate. In this copreciptiation target, iodine concentration was diluted, causing a reduced signal intensities of ^{127}I and ^{129}I in AMS measurement [23,24]. In this work, 0.20 mg spiked ^{127}I carrier (iodide) and chlorine from aerosol samples itself were used to coprecipitate ^{129}I from trapping solution of aerosol, and the amount of coprecipitate is about 2-3 mg without washing using diluted $NH_3 \cdot H_2O$. The measured ^{127}I currents in aerosol samples fell within 20-70 nA with an exception low (3.9 nA) sample. Even though about one order of magnitude lower than those of AgI precipitate, the measured $^{127}I^{5+}$ current (20-70 nA) is relative stable for ^{129}I measurement (Table 2), implying 0.2 mg ^{127}I carrier is sufficient for AMS measurement.

While in the case of high chloride concentration in aerosol samples, it is hard to control the precipitate amount into 2-3 mg, which will greatly decrease ^{129}I counts and ^{127}I current. In order to get rid of excessive chloride from the precipitate, diluted ammonium hydroxide (5%-20% v/v) is used to dissolve AgCl and leave AgI in the precipitate. With this step, ^{127}I currents in aerosol samples significantly increased to 210-400 nA, which is comparable to that of AgI standard (660 nA) (Table 2). Therefore, in the following experiment, all AgI-AgCl precipitate was treated with diluted ammonium hydroxide to ensure high ^{129}I counts and ^{127}I current intensity.

Table 2. The AMS measured ^{127}I currents and $^{129}I/^{127}I$ ratios for the AgI precipitate and AgI-AgCl coprecipitation of standards and aerosol samples with and without treatment of ammonium hydroxide

Holder No.	**Sample type**	**Diluted ammonium washing**	**^{127}I carrier, mg**	**Cl addition, mg**	**^{127}I Current, nA**	**$^{129}I/^{127}I$ ratio, $\times 10^{-12}$**
D7915 *	AgI Standards	No	2.0	0	660 ± 230	104 ± 2

D7917 *	AgI-AgCl Standards	No	1.0	5.0	62.3 ± 4.4	100 ± 3
D7543	Procedure blank	No	0.20	0.50	69.9 ± 2.7	3.4 ± 0.5
D7544	Aerosol	No	0.20	0	47.1 ± 1.9	48.0 ± 2.6
D7545	Aerosol	No	0.20	0	46.6 ± 2.5	23.0 ± 1.6
D7547	Aerosol	No	0.20	0	3.90 ± 0.1	91.4 ± 9.2
D7548	Aerosol	No	0.20	0	53.8 ± 2.4	143 ± 5
D7549	Aerosol	No	0.20	0	51.7 ± 2.4	507 ± 11
D7550	Aerosol	No	0.20	0	20.0 ± 1.3	93.5 ± 4.3
D9218	Aerosol	Yes	0.20	0	292 ± 21	43.9 ± 0.5
D9219	Aerosol	Yes	0.20	0	358 ± 53	67.1 ± 0.8
D9220	Aerosol	Yes	0.20	0	221 ± 33	220 ± 2
D9221	Aerosol	Yes	0.20	0	322 ± 23	240 ± 2
D9222	Aerosol	Yes	0.20	0	291 ± 52	281 ± 3
D9223	Aerosol	Yes	0.20	0	400 ± 60	267 ± 2
D9224	Aerosol	Yes	0.20	0	209 ± 58	214 ± 3

* All the $^{129}I/^{127}I$ ratios are direct instrumental results without calibration. $^{129}I/^{127}I$ ratios of the AgI and AgI-AgCl standard is $(107.2 \pm 3.5) \times 10^{-12}$.

Figure 3 and 4 show the measured AMS spectrums of ^{129}I in AgI and AgI-AgCl standards, as well as blank and samples of aerosol, it show although count rate of ^{129}I is apparently decreased in AgI-AgCl target, but no significant interference was observed in the spectrum of both AgI-AgCl coprecipitate and AgI precipitate (Figure 3). No impurities on the spectrum is found by comparing the aerosol procedural blank and aerosol sample (Figure 4).

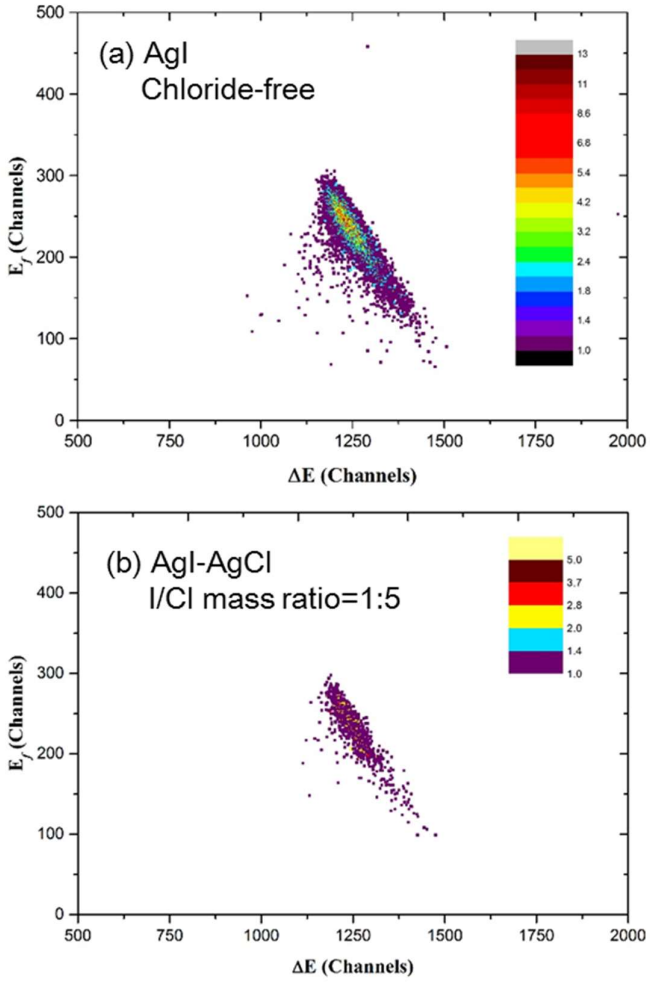


Figure 3. Energy spectrum of ^{129}I on 3 MV AMS (HVEE) for standard with $^{129}I/^{127}I$ ratio of 1.072×10^{-10} (a) AgI standard sample and (b) AgI-AgCl coprecipitation standard sample with the mass ratio of 1: 5 for iodide/chloride. There are no additional impurity on the spectrum of AgI-AgCl in comparison to AgI spectrum. Addition of chloride does not introduce any impurity.

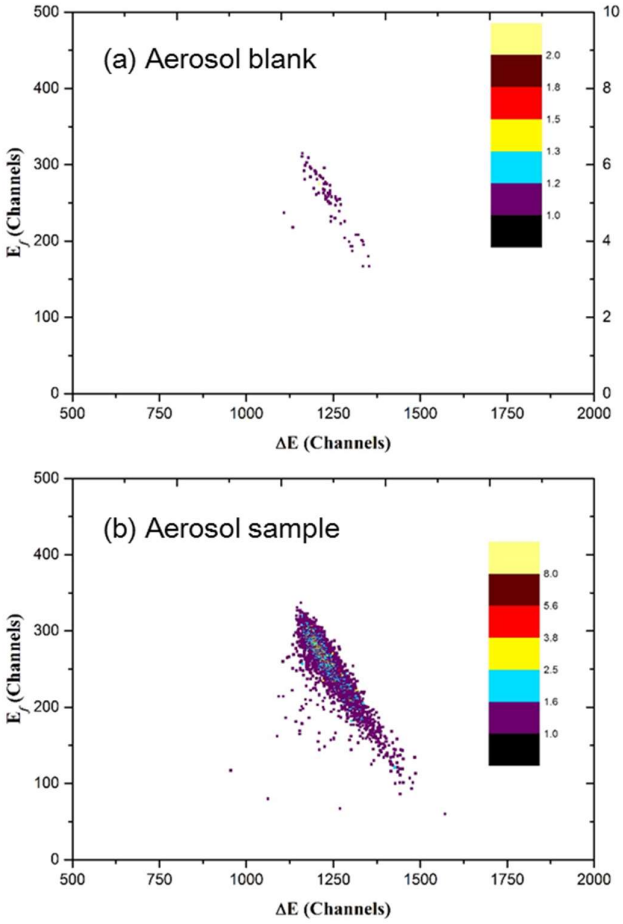


Figure 4. Energy spectrum of ^{129}I in the form of AgI-AgCl coprecipitation on 3 MV AMS (HVEE) for (a) aerosol procedural blank and (b) aerosol sample with addition of 0.2 mg ^{127}I carrier for both targets and 0.5 mg chloride only for procedural blank.

3.5 Figures of merit and method validation

Limit of Detection. The detection limit was calculated as 3 times standard deviation (σ_0) of blank for a certain amount of measurements, i.e. DL = $3\sigma_0$. Procedure blanks were prepared using the same conditions as samples. The measured ^{127}I and ^{129}I concentration and ^{129}I/^{127}I ratio of the procedural blanks (n=7) are 43.6 ± 7.4 ng/g filter, (3.8 ± 2.6) × 10^6 atoms/g and (4.9 ± 2.4) × 10^{-12}, respectively. Detection limit of ^{127}I can be calculated as 22.2 ng/g for this method, about one order of magnitude higher than that of the previously reported method for polypropylene filter (2.1 ng/g filter)

[14]. The glass fiber filter used in this work has been baked at 105°C for 24 h, while this treatment is not helpful to decrease the procedural blank. Detection limit of ^{129}I is calculated to be 7.8×10^6 atoms/g for aerosol using glass fiber, pyrolysis-AgI-AgCl coprecipitation separation and 0.20 mg ^{127}I carrier. This is comparable to that previously reported detection limit (7.1×10^6 atoms/g filter) for polypropylene filter [14]. Considering air flux of 600 m^3 per gram glass fiber filter, detection limits for ^{127}I and ^{129}I concentrations in air can be calculated to be 0.037 ng/m^3 and 1.3×10^4 atoms/m^3, respectively. Toyama et al. has reported ^{127}I concentrations well beyond 2 ng/m^3 and $^{129}I/^{127}I$ ratios of (8-1000) $\times 10^{-10}$ in atmospheric fallout samples collected in Japan from 1963 to 2005 [25]. Assuming a similar level of ^{129}I and ^{127}I in remote areas from nuclear facilities in Asia, the minimum sample size for the determination of 129I can estimated to be 1000 m^3 (corresponding to 1.7 g glass fiber filter in this study) in the case of the lowest $^{129}I/^{127}I$ ratios of 8×10^{-10}, while at least 2800 m^3 air is necessary when using the previously reported method (alkaline ashing in combination with solvent extraction with 1.0 mg ^{127}I carrier). With this method, the amount of sample size can be reduced by a factor of 3.

Method validation. Since no aerosol standard for ^{129}I determination is available, a simulated sample with similar matrix was prepared by mixing IAEA 375 soil samples with blank glass fiber filter. With the optimized method presented above, the measured ^{129}I concentration (0.0018 ± 0.0001 Bq/kg, corresponding to (1.26 ± 0.02) × 10^{12} atoms/kg, n=5) is in good agreement with the recommended value (0.0017 ± 0.0004 Bq/kg, i.e. (1.21 ± 0.29) × 10^{12} atoms/kg), suggesting that the developed method is accurate for determination of ^{129}I in aerosols on glass fiber filter.

Analytical capacity. For analyzing the aerosol samples for ^{129}I, the pyrolysis and precipitate preparation take 3 h (for one batch of four samples) and 2 h (for eight samples), respectively. Two batches of samples (eight samples) can be easily completed in one day. which is much efficient compared to alkali fusion method (more than two days for one batch samples (< 20 samples)). Furthermore, the experimental operation is convenient. In contrast to other methods [14,15], the method developed in this study greatly reducing the labor intensity by saving the steps, for example alkaline ashing,

solution extraction, filtration, solvent extraction.

3.6 Concentrations of ^{129}I and ^{127}I in aerosols from Xi'an

Four aerosol samples collected in Xi'an, China in 2007 were analyzed using the established method. The results (Table 3) show that ^{127}I concentrations in the four aerosol samples vary from 3.70 ng/m^3 to 18.3 ng/m^3, which fell within the typical range of iodine concentrations in aerosol from open ocean and coastal sites (0.03−24 ng/m^3), but much higher than those in continental site (0.07-3.3 ng/m^3, i.e. South Pole and Eastern Treansvaal) [1]. Relatively higher aerosol ^{127}I concentrations were observed in the winter of 2007. The ^{129}I concentrations and $^{129}I/^{127}I$ atomic ratios in the aerosol samples are in the range of (0.38-5.19) × 10^5 atoms/m^3 and (21.7-252) × 10^{-10}, respectively, which are comparable with those in Spain and Japan before the Fukushima accident [25,26], about 1-2 orders of magnitude lower than those in Northern Europe and Japan after the Fukushima accident [6,13,27]. The variation of concentration of iodine isotopes in aerosol in Xi'an, China might be attributed to the Westerly, Eastern Asian summer and winter monsoon, and fossil fuel combustion [28–30].

Table 3. Concentrations of ^{127}I and ^{129}I and $^{129}I/^{127}I$ ratios in aerosols from Xi'an, China

采样日期	Weather	^{127}I in aerosol, ng/m^3	^{129}I concentration, ×10^5 atoms/m^3	$^{129}I/^{127}I$ atomic ratio, ×10^{-10}
2017-6-25	Sunny	3.70 ± 0.08	0.38 ± 0.02	21.7 ± 1.1
2017-8-16	Sunny	4.35 ± 0.07	5.19 ± 0.56	252 ± 27
2017-11-7	Sunny	9.01 ± 0.05	1.14 ± 0.07	26.7 ± 1.7
2017-12-28	Sunny	18.3 ± 1.0	3.46 ± 0.32	39.9 ± 4.3

Conclusions and perspectives

An accurate analytical method for determination of ^{129}I in aerosol samples was developed by separation of iodine isotopes using pyrolysis and AgI-AgCl coprecipitation in combination with AMS measurement. Pyrolysis behaviors of four species of iodine were investigated, and shows different from each other relating to their physicochemical properties. But all iodine species in aerosols show the same

recovery as iodide-125 tracer in the atmosphere of oxygen under 800°C. The iodate release during pyrolysis might be attributed to decomposition of iodate into iodide and oxygen at high temperature. The low ^{127}I current owing to addition of chloride as non-isotopic carrier can be overcome by removing excessive AgCl with diluted ammonium hydroxide.

This developed method is efficient, less labor force and smaller sample sized required (a maximum of 1000 m^3 for ^{129}I level in Asia), which makes atmospheric ^{129}I study with highly temporal resolution and better understand atmospheric processes of stable iodine and radioactive iodine possible. Concentrations of ^{129}I and ^{127}I, and $^{129}I/^{127}I$ ratios in aerosols from Xi'an, China were determined to be 3.70 -18.3 ng/m^3, (0.38-5.19) × 10^5 atoms/m^3 and (21.7-252) × 10^{-10}, respectively. Long-term observation on aerosol ^{129}I and ^{127}I concentration in China is on the way to investigate source, level and temporal variation of iodine isotopes, which will provide a useful data and sensitive tool for evaluation of nuclear environmental safety.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the Supplementary materials.

Reference

[1] A. Saiz-Lopez, J.C. Gómez Martín, J.M.C. Plane, R.W. Saunders, A.R. Baker, R. Von Glasow,

L.J. Carpenter, G. McFiggans, Atmospheric chemistry of iodine, Chem. Rev. 112 (2012) 1773–1804.

[2] M. Sipilä, N. Sarnela, T. Jokinen, H. Henschel, H. Junninen, J. Kontkanen, S. Richters, J. Kangasluoma, A. Franchin, O. Peräkylä, M.P. Rissanen, M. Ehn, H. Vehkamäki, T. Kurten, T. Berndt, T. Petäjä, D. Worsnop, D. Ceburnis, V.-M. Kerminen, M. Kulmala, C. O'Dowd, Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3, Nature. 537 (2016) 532. http://dx.doi.org/10.1038/nature19314.

[3] M. Honda, H. Matsuzaki, Y. Miyake, Y. Maejima, T. Yamagata, H. Nagai, Depth profile and mobility of 129I and 137Cs in soil originating from the Fukushima Dai-ichi Nuclear Power Plant accident, J. Environ. Radioact. 146 (2015) 35–43. doi:10.1016/j.jenvrad.2015.03.029.

[4] S. Xu, L. Zhang, S.P.H.T. Freeman, X. Hou, A. Watanabe, D.C.W. Sanderson, A. Cresswell, K. Yamaguchi, Iodine isotopes in precipitation: Four-year time series variations before and after 2011 Fukushima nuclear accident, J. Environ. Radioact. 155–156 (2016). doi:10.1016/j.jenvrad.2016.02.011.

[5] X. Hou, P.P. Povinec, L. Zhang, K. Shi, D. Biddulph, C.-C. Chang, Y. Fan, R. Golser, Y. Hou, M. Ješkovský, A.J.T. Jull, Q. Liu, M. Luo, P. Steier, W. Zhou, Iodine-129 in seawater offshore fukushima: Distribution, inorganic speciation, sources, and budget, Environ. Sci. Technol. 47 (2013). doi:10.1021/es304460k.

[6] S. Xu, L. Zhang, S.P.H.T. Freeman, X. Hou, Y. Shibata, D. Sanderson, A. Cresswell, T. Doi, A. Tanaka, Speciation of Radiocesium and Radioiodine in Aerosols from Tsukuba after the Fukushima Nuclear Accident, Environ. Sci. Technol. 49 (2015) 1017–1024. doi:10.1021/es504431w.

[7] T. Doi, K. Masumoto, A. Toyoda, A. Tanaka, Y. Shibata, K. Hirose, Anthropogenic radionuclides in the atmosphere observed at Tsukuba: characteristics of the radionuclides derived from Fukushima, J. Environ. Radioact. 122 (2013) 55–62. doi:http://dx.doi.org/10.1016/j.jenvrad.2013.02.001.

[8] T. Matsunaka, K. Sasa, K. Sueki, T. Takahashi, Y. Satou, M. Matsumura, N. Kinoshita, J. ichi Kitagawa, H. Matsuzaki, Pre- and post-accident 129I and 137Cs levels, and 129I/137Cs ratios in soil near the Fukushima Dai-ichi Nuclear Power Plant, Japan, J. Environ. Radioact. 151 (2016) 209–217. doi:10.1016/j.jenvrad.2015.10.010.

[9] T. Jabbar, G. Wallner, P. Steier, A review on 129I analysis in air, J. Environ. Radioact. 126 (2013) 45–54.

[10] T. Jabbar, P. Steier, G. Wallner, A. Priller, N. Kandler, A. Kaiser, Iodine Isotopes (127I and 129I) in Aerosols at High Altitude Alp Stations, Environ.Sci.Technol. 46 (2012) 8637–8644.

[11] T. Jabbar, G. Wallner, P. Steier, C. Katzlberger, N. Kandler, Retrospective measurements of airborne 129Iodine in Austria, J. Environ. Radioact. 112 (2012) 90–95.

[12] F.J. Santos, J.M. López-Gutiérrez, E. Chamizo, M. García-León, H.A. Synal, Advances on the determination of atmospheric 129I by accelerator mass spectrometry (AMS), Nucl.Instrum.Meth.B. 249 (2006) 772–775.

[13] L. Zhang, X. Hou, S. Xu, Speciation of 127I and 129I in atmospheric aerosols at Risø, Denmark: Insight into sources of iodine isotopes and their species transformations, Atmos.Chem.Phys. 16 (2016) 1971–1985.

[14] L. Zhang, X. Hou, S. Xu, Speciation Analysis of 129I and 127I in Aerosols Using Sequential Extraction and Mass Spectrometry Detection, Anal. Chem. 87 (2015) 6937–6944. doi:10.1021/acs.analchem.5b01555.

[15] F.J. Santos, J.M. López-Gutiérrez, M. García-León, M. Suter, H.A. Synal, Determination of 129I/127I in aerosol samples in Seville (Spain), J. Environ. Radioact. 84 (2005) 103–109.

[16] A. Daraoui, B. Riebe, C. Walther, H. Wershofen, C. Schlosser, C. Vockenhuber, H.A. Synal, Concentrations of iodine isotopes (129I and 127I) and their isotopic ratios in aerosol samples from Northern Germany, J. Environ. Radioact. 154 (2016) 101–108. doi:10.1016/j.jenvrad.2016.01.021.

[17] X. Hou, W. Zhou, N. Chen, L. Zhang, Q. Liu, M. Luo, Y. Fan, W. Liang, Y. Fu, Determination of ultralow level 129I/127I in natural samples by separation of microgram carrier free iodine and accelerator mass spectrometry detection, Anal. Chem. 82 (2010). doi:10.1021/ac101558k.

[18] S. Xing, X. Hou, A. Aldahan, G. Possnert, Speciation analysis of 129I in seawater using coprecipitation and accelerator mass spectrometry and its applications, J. Radioanal. Nucl. Chem. 311 (2017) 833–841. doi:10.1007/s10967-016-5060-6.

[19] M. Luo, W. Zhou, X. Hou, N. Chen, L. Zhang, Q. LIU, C. He, Y. Fan, W. LIANG, Z. Wang, Y. Fu, Determination of Low Level 129I in Soil Samples Using Coprecipitation Separation of Carrier Free Iodine and Accelerator Mass Spectrometry Measurement, Chinese J. Anal. Chem.

39 (2011) 193–197. doi:10.1016/S1872-2040(10)60416-1.

[20] X. Hou, Y. Wang, Determination of ultra-low level 129I in vegetation using pyrolysis for iodine separation and accelerator mass spectrometry measurement, J. Anal. At. Spectrom. 31 (2016) 1298–1310. doi:10.1039/C6JA00029K.

[21] Database of Physico-chemical properties of substance, Http://Chemister.Ru/Database/Properties-En.Php?Dbid=1&id=759. (n.d.).

[22] K. Muraleedharan, Thermal decomposition kinetics of potassium iodate, J. Therm. Anal. Calorim. 109 (2012) 237–245.

[23] X. Hou, W.J. Zhou, N. Chen, L. Zhang, Q. Liu, M. Luo, Y. Fan, W. Liang, Y. Fu, Determination of Ultralow Level 129I/127I in Natural Samples by Separation of Microgram Carrier Free Iodine and Accelerator Mass Spectrometry Detection, Anal.Chem. 82 (2010) 7713–7721. doi:10.1021/ac101558k.

[24] L. Zhang, X. Hou, W. Zhou, N. Chen, Q. Liu, M. Luo, Y. Fan, Y. Fu, Performance of Accelerator Mass Spectrometry for 129I using AgI-AgCl carrier-free coprecipitation, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 294 (2013) 276–280. doi:10.1016/j.nimb.2012.06.023.

[25] C. Toyama, Y. Muramatsu, Y. Igarashi, M. Aoyama, H. Matsuzaki, Atmospheric fallout of 129I in Japan before the Fukushima accident: Regional and global contributions (1963-2005), Environ. Sci. Technol. 47 (2013) 8383–8390. doi:10.1021/es401596z.

[26] J.M. López-Gutiérrez, M. García-León, C. Schnabel1, A. Schmidt, R. Michel, H.A. Synal, M. Suter, Determination of 129I in atmospheric samples by accelerator mass spectrometry, Appl.Radial.Isot. 51 (1999) 315–322.

[27] E. Englund, A. Aldahan, X. Hou, G. Possnert, C. Soderstrom, Iodine (I-129 and I-127) in aerosols from northern Europe, Nucl.Instrum.Meth.B. 268 (2010) 1139–1141.

[28] L. Zhang, X. Hou, P. Cheng, N. Chen, Y. Fan, Q. Liu, Impact of North Korean nuclear weapons test on 3 September, 2017 on inland China traced by ^{14}C and ^{129}I, J. Radioanal. Nucl. Chem. (2018). doi:10.1007/s10967-018-5747-y.

[29] L. Zhang, X. Hou, H. Li, X. Xu, A 60-year record of 129 I in Taal Lake sediments (Philippines): Influence of human nuclear activities at low latitude region, Chemosphere. (2017). doi:10.1016/j.chemosphere.2017.11.134.

[30] Y. Fan, X. Hou, W. Zhou, G. Liu, I record of nuclear activities in marine sediment core from Jiaozhou Bay in China, J. Environ. Radioact. 154 (2016) 15–24. doi:10.1016/j.jenvrad.2016.01.008.

Supplementary material

The supplementary material includes three tables and one figure.

Table S1 Combustion program for ^{129}I separation from aerosol on glass fiber filter

Step	segment type	Temperature, °C	duration	Ramp rate	Gas and flow rate
1	Time	20-250	20 min	11.5°C/min	
2	dwell	250	10 min		N_2, 0.1 L/min;
3	Time	250-400	30 min	5°C/min	O_2, 0.1 L/min
4	dwell	400	20 min		
5	time	400-(700-900)°C	40 min	7.5-12.5°C/min	O_2, 0.2 L/min
6	dwell	(700-900) °C	1-3 hours		

Table S2 Operating parameters of the AMS (3 MV, HVEE, the Netherlands)

AMS parameters	3 MV (HVEE)
Energy of Cs-sputter negative ion source	35 keV
Bouncer frequency	100 Hz
Injection time of ion	Mass 129: 9 ms; Mass 127: 100 μs
stripper gas	Ar
Acceleration voltage	2.5 MeV
Charge state of iodine	+5
Mass resolution M/ΔM for ^{129}I	820
Stripping yield of I^{5+}	3.6-3.8%
Iodine ion current in the Faraday cup	0-100 nA for AgI-AgCl coprecipitation targets
	0-1 μA for AgI precipitate targets
Energy resolution E/ΔE of the cylindrical electrostatic analyzer	750
Mass resolution M/ΔM of the 30° deflection magnet	175
Measurement time per cycle	5 min per sample

Cycle number	6 cycles

Table S3 Operating parameters of the ICP-MS/MS (8800 series, Agilent)

ICP-MS parameters	8800 series (Agilent)
RF power	1480 W
Sampling depth	4.0 mm
Plasma gas	15 L min^{-1}
Auxiliary gas	0.8 L min^{-1}
Carrier gas	0.9 L min^{-1}
Nebulizer	MicroMist
Data acquisition mode	Full quantitative data collection
Analysed isotopes	^{127}I, ^{133}Cs
Analysis mode	Single quadrupole, no collision/reaction gas
Dwell time	0.1 s
Repeat of measurements	3
CeO/Ce	< 2.0 %
Ce^{2+}/Ce	< 3.0 %
Spray chamber temperature	2.0°C

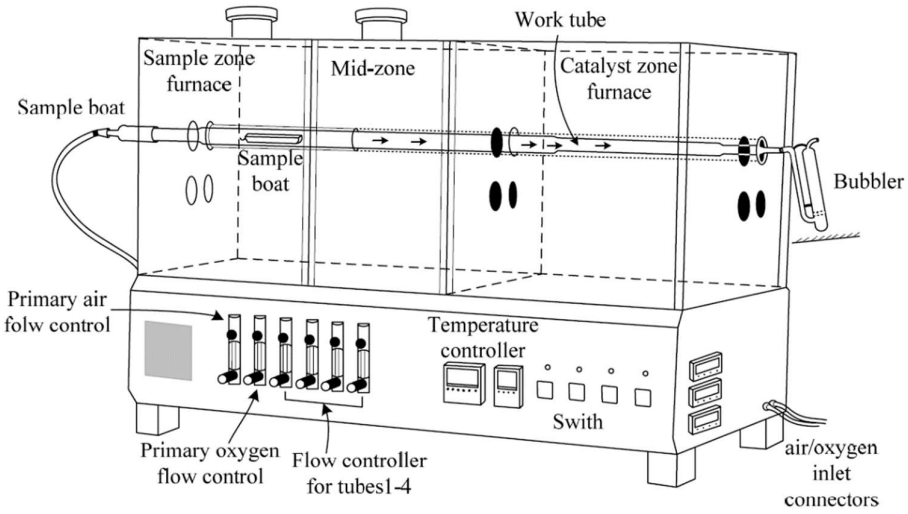

Figure S1 Schematic diagram of the pyrolyser-4 TrioTM furnace